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**WO 02/092686 A1**

(54) Title: PVC STABILISERS

(57) **Abstract:** Object: to obtain a stabiliser for rigid and semirigid PVC free from heavy metals (Ba, Cd, Pb, Sn) and zinc, with excellent thermal stability and good colour fastness. Constitution: the composition comprises as fundamental component a) a substance selected from the group consisting of crystalline hydrotalcites, crystalline or amorphous zeolites previously treated with perchloric acid or metal perchlorates, b) a carboxylated metallic salt with M belonging to alkaline or alkaline earth groups in association with substances belonging to c) a group of organic costabilisers and to d) a group of antioxidants.

## PVC STABILISERS

### Field of the invention

The present invention refers to a stabilising composition for halogenated polymers and in particular for PVC. The present invention especially refers to a composition of an inorganic stabiliser free from heavy metals and zinc, including--as main component--a zeolite perchlorate or a hydrotalcite perchlorate in synergistic association with metal carboxylates, organic costabilisers and organic antioxidants.

### Prior art

A great number of PVC stabilisers have been well-known for a long time. The main stabilisers are based on lead derivatives, organometallic compounds of tin, mixtures of metallic soaps and organic compounds.

Lead derivatives are largely used and include inorganic salts (e.g. lead tribasic sulphate, lead dibasic phosphite, etc.) and lead soaps, such as for example stearates, laurates, etc.

Organostannic stabilisers may be alkyl-tin mercaptides or carboxylates and are mainly used in the stabilisation of rigid PVC.

The compounds consisting of metallic soaps mixtures are based on combinations of salts of alkaline or alkaline earth metal carboxylic acids, such as for example barium-zinc or calcium-zinc derivatives; these last are a valid alternative to the conventional systems based on heavy metals and their consumption is constantly growing.

Conventional stabilising systems include perchlorates in the various forms known, e.g. supported on materials, such as zeolites, calcium silicate, hydrotalcites, or bound to hydrotalcites through a chemical reaction.

Perchlorates are especially used in PVC stabilisers for car's interior, where PVC is in contact with polyurethanes. The presence of perchlorates brings about an excellent thermal stability and, obviously, slows down the degradation derived from the contact with amines. Examples illustrating said properties are described in JP04173854.

JP8283499 discloses that, thanks to the presence in the stabilising system of perchlorates in association with zeolites or hydrotalcites treated with perchlorates,

PVC--when used in powder formulations for moulding--exhibits good gelling properties and is easily removed from the mould.

As described in JP7149979, the resistance to ageing in various conventional processes increases in the presence of a stabilising system including ammonium

5 perchlorate in association with zeolites or hydrotalcites treated with perchlorates.

To solve explosiveness problems and provide safe handling properties, JP4050250 proposes the use of metallic perchlorates with zeolites or hydrotalcites.

EP0286887 discloses that the addition of polydihydropyridine to stabilising

10 systems based on calcium and zinc brings about an increased stabilising efficiency.

All the aforesaid systems may contain heavy metals or zinc. That is why the present ever growing interest in stabilising systems free from heavy metals and zinc has spurred the development of new systems.

15 US5543449 discloses that highly stable plastified PVC can be obtained using a perchlorate and an epoxy compound, and not lead or cadmium.

US5859100 proposes uracil derivatives as fundamental components of a rigid or semirigid PVC composition essentially free from heavy metals.

### **Summary of the invention**

20 It is an object of the present invention to provide a stabilising composition free from heavy metals and zinc meeting the most recent ecological requirements.

The stabiliser composition comprises 1) zeolite perchlorate or hydrotalcite perchlorate, 2) a fatty acid salt of alkaline or alkaline earth metals, 3) an organic antioxidant and 4) an organic costabiliser. In the specific combination of the four

25 components, the new system allows the obtainment of excellent stabilising properties in the absence of heavy metals (barium, cadmium, lead, tin) and in the absence of zinc derivatives.

Now, it has been found that rigid or semirigid PVC, stabilised by means of a mixture as the one described, exhibits an excellent thermal stability, a satisfactory

30 initial colour, and a good colour fastness.

Additives known for polyvinylchlorides can be added to the stabiliser composition of the present invention according to the formulation known, e.g. lubricants such

as paraffin, oxidised waxes, polyethylene wax, microcrystalline wax, lubricant esters.

It has surprisingly been found that the primary stabiliser, zeolite or hydrotalcite, combined with perchloric acid or perchlorates is highly effective--thanks to the particular combination of components--for maintaining a good initial colour fastness and an excellent thermal stability, also in the absence of zinc derivatives.

#### **Detailed description of the invention**

##### Zeolite perchlorate

Zeolites may be represented by general formula (I)



where a is the M cation charge,

M is an element of the first or second main group, in particular Na, K, Mg,

q is a number equal to or greater than 2,

q:r is a number equal to or greater than 0.4, preferably ranging from 0.4 to 10.5,

and

w is a number ranging from 0 to 300.

The zeolites that can be used according to the present invention are described in "Atlas of Zeolite Structure Types", W. M. Meier and D. H. Olson, Butterworths, 3rd Edition, 1992.

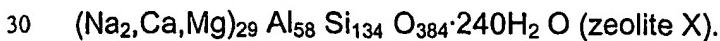
The zeolites whose particle size is predominantly in the range from 0.5 to 10 micron are particularly preferred.

The preferred known zeolites have a cavity of 3-5 Å in average actual diameter and can be prepared according to methods known in the art.

Particularly preferred are the zeolites of type NaA, which have a cavity of 4 Å in average actual diameter. Therefore, they are known as zeolites 4A and are represented by formula



Particularly preferred are also the zeolites of general formula (I), known as zeolites X, represented by formula



The zeolite compound including ion perchlorate used in the present invention is the compound obtained by contact of a zeolite of the type represented in formula

(I) with perchloric acid or, in particular, with metallic perchlorate, where M belongs to the group consisting of alkaline or alkaline earth metals, M=Na, K, Mg being particularly preferred.

- Particularly preferred are the zeolite perchlorates whose particle size is  
5 predominantly in the range from 0.5 to 10 micron.

#### Hydrotalcite perchlorate

Hydrotalcite-type compounds are generally represented by formula (II)



where m is a positive number and x is a number satisfying the equation  $0 < x \leq 0.5$ .

- 10 The hydrotalcite compound with ion perchlorate utilised in the present invention is the compound obtained through an exchange reaction of the ion carbonate of a hydrotalcite of the type represented by formula (III)



with an ion perchlorate as represented by formula (IV)

- 15  $\text{Mg}_4\text{Al}_2(\text{OH})_{12} (\text{ClO}_4)_x (\text{CO}_3)_{1-x/2} \cdot m\text{H}_2\text{O} \text{ (IV)}$

where m =0-6 and x is a number satisfying the equation  $1 < x \leq 2$ .

An example of said product is Alcamizer 5 (Kyowa).

#### Metallic perchlorates

Out of the metallic perchlorates that may be utilised in the present invention,

- 20 sodium perchlorate, potassium perchlorate, magnesium perchlorate are preferred.

The sodium perchlorate used is the one commercially available; titre: 84 to 87%. It contains crystallisation water as  $(\text{NaClO}_4 \cdot 1\text{H}_2\text{O})$ .

The potassium perchlorate used is the one commercially available; titre: 98 to 99%.

- 25 The magnesium perchlorate used is the one commercially available; titre: 98 to 99%.

#### Metallic soaps

All metallic soaps commonly used as PVC stabilisers may be utilised in the

present invention. By way of example, it is possible to use salts of long-chain

- 30 saturated or unsaturated fatty acids containing 12 to 22 carbon atoms, especially 14 to 18 carbon atoms, with alkaline or alkaline earth metals, salts of long-chain saturated fatty acids containing 12 to 22 carbon atoms, especially 14 to 18 carbon

atoms, of which one at least is substituted with an OH group, and other salts, such as for example salts of abietic acids.

Li, Na, K, Mg, Ca salts of the aforementioned fatty acids, in particular of palmitic, stearic, lauric, oleic, hydroxystearic acids, are preferably used as metallic soaps.

5 Organic costabiliser

Organic costabilisers are used to increase the stabilising system efficiency.  $\beta$ -Diketonic compounds and dihydropyridines or polydihydropyridines are especially used.

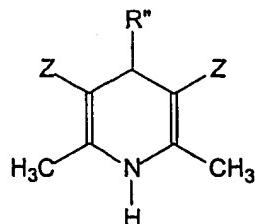
1.  $\beta$ -diketonic compounds. The 1,3 dicarbonyl compounds that can be used are  
10 linear or cyclic dicarbonyl compounds, preferably the dicarbonyl compounds of formula



- where R<sub>1</sub> is C<sub>1</sub>-C<sub>22</sub> alkyl, C<sub>5</sub>-C<sub>10</sub> hydroxyalkyl, C<sub>3</sub>-C<sub>7</sub> alkenyl, phenyl, OH-, C<sub>1</sub>-C<sub>4</sub> alkyl-, C<sub>1</sub>-C<sub>4</sub> haloalkyl-substituted phenyl, C<sub>7</sub>-C<sub>10</sub> phenylalkyl, C<sub>5</sub>-C<sub>12</sub> cycloalkyl,  
15 C<sub>1</sub>-C<sub>4</sub> alkyl-substituted C<sub>5</sub>-C<sub>12</sub> cycloalkyl, R<sub>2</sub> is hydrogen, C<sub>1</sub>-C<sub>8</sub> alkyl, C<sub>3</sub>-C<sub>7</sub> alkenyl, C<sub>2</sub>-C<sub>12</sub> phenyl, C<sub>7</sub>-C<sub>12</sub> alkylphenyl, C<sub>7</sub>-C<sub>10</sub> phenylalkyl, R<sub>3</sub> has the same meaning as R<sub>1</sub>.

Dibenzoylmethane, stearoylbenzoylmethane and dehydroacetic acid are particularly preferred.

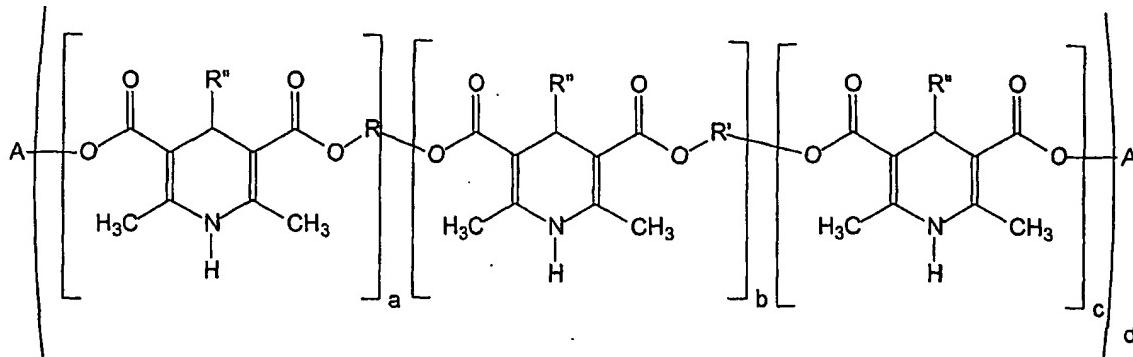
- 20 2. Dihydropyridine (DHP) or polydihydropyridine (polyDHP). The monomeric dihydropyridine derivatives that may be advantageously used are carboxyl acid esters of general formula



- where Z is CO<sub>2</sub>C<sub>2</sub>H<sub>5</sub>, CO<sub>2</sub>(n-C<sub>12</sub>H<sub>25</sub>), R'' is hydrogen or C<sub>1</sub>-C<sub>18</sub> alkyl or C<sub>2</sub>-C<sub>18</sub> alkoxy carbonyl or C<sub>6</sub>-C<sub>10</sub> aryl. 3-Bisdodecyloxycarbonyl-2,6-dimethyl-1,4-dihydropyridine, available under the trademark Stavinor D507 from Atochem, is

particularly preferred.

Suitable polydihydropyridines are especially the compounds of formula



where A is non-substituted C<sub>1</sub>-C<sub>22</sub> alkyl or C<sub>1</sub>-C<sub>22</sub> alkyl substituted with C<sub>1</sub>-C<sub>18</sub> alkoxy, C<sub>1</sub>-C<sub>18</sub> alkylthio, hydroxy, acryloyloxy, meta-acryloyloxy, halogen, phenyl,

5 a and b are numbers from 0 to 20,

c is 0 or 1,

d is a number from 1 to 6 and conditions d(a+b+c)>1 and a+b>0 are respected,

R and R' are each methylene or phenylene or an alkylene of type

(—C<sub>p</sub>H<sub>2p</sub>—X—)<sub>t</sub>C<sub>p</sub>H<sub>2p</sub>—,

10 p is a number from 2 to 18,

t is a number from 0 to 10,

X is oxygen or sulphur,

R'' is hydrogen or C<sub>1</sub>-C<sub>18</sub> alkyl or C<sub>2</sub>-C<sub>18</sub> alkoxy carbonyl or C<sub>6</sub>-C<sub>10</sub> aryl. Particularly preferred is thiodiethylene-bis[5-methoxycarbonyl-2,6-dimethyl-1,4-

15 dihydropyridine-3-carboxylate] available under the trademark Synesal M from Lagor.

#### Organic antioxidant

The organic antioxidants used in the present invention are selected among the ones already known as additives for plastic materials. A synergistic effect with the

20 aforementioned components is exhibited by the antioxidants, whose valid examples belong to the following classes:

1. Alkylidenebisphenols, e.g. 2,2'-methylene-bis(6-tert-butyl-4-methylphenol), 2,2'-methylene-bis(6-tert-butyl-4-ethylphenol),

2,2'-methylene-bis[4-methyl-6-( $\alpha$ -methylcyclohexyl)phenol], 2,2'-methylene-bis(4-methyl-6-cyclohexylphenol), 2,2'-

25 methylene-bis(6-nonyl-4-methylphenol), 2,2'-methylene-bis(4,6-di-tert-butylphenol),

2,2'-ethylidene-bis(4,6-di-ter-butylphenol), 2,2'-ethylidene-bis(6-ter-butyl-4-isobutylphenol), 2,2'-methylene-bis[6-( $\alpha$ -methylbenzyl)-4-nonylphenol], 2,2'-methylene-bis[6-( $\alpha,\alpha$ -dimethylbenzyl)-4-nonylphenol], 4,4'-methylene-bis(2,6-di-ter-butylphenol), 4,4'-methylene-bis(6-ter-butyl-2-methylphenol), 1,1-bis(5-ter-butyl-4-hydroxy-2-methylphenyl)butane, 2,6-bis(3-ter-butyl-5-methyl-2-hydroxybenzyl)-4-methylphenol, 1,1,3-tris(5-ter-butyl-4-hydroxy-2-methylphenyl)butane, 1,1-bis(5-ter-butyl-4-hydroxy-2-methylphenyl)-3-n-dodecylmercaptopbutane, ethylene glycol bis[3,3-bis(3'-ter-butyl-4'-hydroxyphenyl)butyrate], bis(3-ter-butyl-4-hydroxy-5-methylphenyl)dicyclopentadiene, bis[2-(3-ter-butyl-2'-hydroxy-5'-methylbenzyl)-6-ter-butyl-4-methyl-phenyl]terephthalate, 1,1-bis(3,5-dimethyl-2-hydroxyphenyl)butane, 2,2-bis(3,5-di-ter-butyl-4-hydroxyphenyl)propane, 2,2-bis(4-hydroxyphenyl)propane, 2,2-bis(5-ter-butyl-4-hydroxy-2-methylphenyl)-4-n-dodecylmercaptopbutane, 1,1,5,5-tetra-(5-ter-butyl-4-hydroxy-2-methylphenyl)pentane.

**2. Esters of  $\beta$ -(3,5-di-ter-butyl-4-hydroxyphenyl)propionic acid with mono- or poly-alcohols**, e.g. methanol, ethanol, octanol, octadecanol, 1,6-hexanediol, 1,9-nonanediol, ethylene glycol, 1,2-propanediol, neopentyl glycol, thiodiethylene glycol, diethylene glycol, triethylene glycol, pentaerythritol, dipentaerythritol, tris(hydroxyethyl) isocyanurate, N,N'-bis(hydroxyethyl)oxalamide, 3-thioundecanol, 3-thiopentadecanol, trimethylhexanediol, trimethylolpropane, ditrimethylolpropane, 4-hydroxymethyl-1-phospha-2,6,7-trioxabicyclo-[2.2.2]-octane.

**3. Esters of  $\beta$ -(5-ter-butyl-4-hydroxy-3-methylphenyl)propionic acid with mono- or polyalcohols**, e.g. methanol, ethanol, octanol, octadecanol, 1,6-hexanediol, 1,9-nonanediol, ethylene glycol, 1,2-propanediol, neopentyl glycol, thiodiethylene glycol, diethylene glycol, triethylene glycol, pentaerythritol, dipentaerythritol, tris(hydroxyethyl) isocyanurate, N,N'-bis(hydroxyethyl)oxalamide, 3-thioundecanol, 3-thiopentadecanol, trimethylhexanediol, trimethylolpropane, 4-hydroxymethyl-1-phospha-2,6,7-trioxabicyclo-[2.2.2]-octane.

**4. Esters  $\beta$ -(3,5-dicyclohexyl-4-hydroxyphenyl)propionic acid with mono- or polyalcohols**, e.g. methanol, ethanol, octanol, octadecanol, 1,6-hexanediol, 1,9-nonanediol, ethylene glycol, 1,2-propanediol, neopentyl glycol, thiodiethylene

glycol, diethylene glycol, triethylene glycol, pentaerythritol, tris(hydroxyethyl) isocyanurate, N,N'-bis(hydroxyethyl)oxalamide, 3-thioundecanol, trimethyloл propane, 4-hydroxymethyl-1-phospho-2,6,7-trioxabicyclo-[2.2.2]-octane. Particularly preferred are 2,2'-methylene-bis(6-tert-butyl-4-methylphenol), available under the trademark Lowinox 22 M46 from Great Lakes Chem. Corp., and the esters of  $\beta$ -(3,5-di-tert-butyl-4-hydroxyphenyl)propionic acid with octadecanol and with pentaerythritol, available under the trademark Arenox A76 and Arenox A10, respectively, from Reagens.

- Composition
- 10 The typical composition of the stabilising system of the present invention comprises zeolite perchlorate or hydrotalcite perchlorate as main component: the composition is generally comprises 0.3 to 2.0 parts by wt. zeolite perchlorate or hydrotalcite perchlorate, preferably 0.5 to 1.2 parts by wt.; 0.1 to 1 parts by wt. metallic soap, preferably 0.2 to 0.4 parts by wt.; 0.03 to 0.3 parts by wt. organic  
15 costabiliser, preferably 0.05 to 0.15 parts by wt.; 0.03 to 0.3 parts by wt. organic antioxidant, preferably 0.05 to 0.15 parts by wt., in respect of 100 parts by wt. PVC. The absence or an inadequate quantity of one component causes an insufficient performance of the stabiliser, the initial colour and the long-term thermal stability being worse. Mixtures having the composition shown in Table 1  
20 were prepared by homogeneously mixing the components. The mixtures were subjected to calendering, which gave the results reported in the examples.

Table 1

<b>Mixtures composition</b>	
PVC evipol SH6530 <sup>1</sup>	100
Calcium carbonate <sup>2</sup>	2
Lubricant mix <sup>3</sup>	1.4
Stabiliser	( <sup>4</sup> )

**Remarks:** <sup>1</sup>supplied by EVC

5 <sup>2</sup>Omya 90T

<sup>3</sup>paraffinic wax 0.4

microcrystalline wax 0.6

stearic acid 0.4

<sup>4</sup>as shown in tables 2, 4

10 Examples

Static stability tests

With the samples listed in Table 2 (examples: series s) and in Table 4 (comparative examples: series z and c), mixtures with the composition as per Table 1 were prepared.

Table 2

	Stabiliser chemical composition expressed as parts by wt. /100 parts PVC												
	s1	s2	s3	s4	s5	s6	s7	s8	s9	s10	s11	s12	s13
Zeolite perchlorate	0,9			0,9	0,9	0,9	0,9	0,9	0,9	0,9	0,9	0,9	0,9
Hydrotalcite perchlorate <sup>1</sup>		0,9	0,9	0,9								0,9	
Ca Stearate	0,3	0,3					0,3		0,3	0,3	0,3		
Mg Stearate			0,3		0,3			0,3				0,3	
Li Stearate				0,3		0,3							
K Stearate												0,3	
Dehydroacetic acid	0,1	0,1	0,1	0,1			0,1		0,1	0,1			
Dibenzoylmethane					0,1								
Stearoylbenzoylmethane							0,1						
Synesal M <sup>3</sup>									0,1	0,1	0,1	0,1	
Arenox A10	0,1	0,1	0,1	0,1	0,1	0,1	0,1			0,1	0,1	0,1	
Arenox A76								0,1				0,1	
Lowinox 22 M46 <sup>2</sup>									0,1				

Remarks:<sup>1</sup> Alcamizer 5 supplied by Kyowa

<sup>2</sup>supplied by Great Lakes Chem. Corp.

<sup>3</sup>supplied by Lagor

The mixtures were allowed to gel in a calender at 190°C for 5 minutes. Rectangular samples (1x1.5 cm) were cut from each sheet (0.5 mm thick). The samples were placed onto slides and heated in an air circulated oven at 190°C. At 5 regular intervals of 15 min, the samples were withdrawn and the colour variation degree was determined visually. Each estimation was performed according to a standard by the following criterion: 1 = white,...,10 = black (entirely degraded). Intermediate points take into account colour variations, if any, in the yellow, red and green range, caused by partial degradation. The longer the delay in colour 10 variation towards the black, the lower the initial colour variation from the white, the faster is the colour, the better is the stabiliser.

The results obtained from the static stability test shown in Table 3 indicate that the stabiliser has excellent properties of colour fastness and stability.

Table 3

	Static thermal stability at 190°C												
	s1	s2	s3	s4	s5	s6	s7	s8	s9	s10	s11	s12	s13
time 0	2	2	2	2	2	2	2	2	2	2	3	2	3
after 15 min	3	3	3	3	3	2	3	3	3	3	3	4	3
after 30 min	4	3	3	3	4	3	3	4	4	4	5	5	5
after 45 min	4	4	3	4	5	4	4	5	5	4	7	6	6
after 60 min	5	4	3	4	6	5	5	6	5	7	8	7	7
after 75 min	6	5	6	5	7	6	6	7	6	8	9	7	9
after 90 min	7	6	9	6	8	6	7	8	7	8	9	8	9
after 105 min	7	7	10	7	9	7	7	9	8	9	9	8	9
after 120 min	8	7	7	9	7	8	9	8	9	9	10	8	9
after 135 min	8	8	8	9	7	8	9	8	9	8	8		

A comparison of the new stabilising system with the samples having the composition shown in Table 4

Table 4

	Stabiliser chemical composition expressed as parts by wt./100 parts PVC								
	z1	z2	z3	c1	c2	c3	c4	c5	c6
Zeolite A				0,9					
Zeolite perchlorate	0,9		0,9				0,9	0,9	0,9
Hydrotalcite <sup>1</sup>					0,9				
Hydrotalcite perchlorate <sup>2</sup>		0,9							
Ca Stearate	0,3	0,3	0,3	0,3	0,3	0,3		0,3	0,3
Dehydroacetic acid	0,1	0,1		0,1	0,1	0,1	0,1		0,1
Synesal M <sup>3</sup>			0,1						
Arenox A10	0,1	0,1	0,1	0,1	0,1	0,1	0,1	0,1	
Zn stearate	0,3	0,3	0,3						

Remarks:<sup>1</sup> Alcamizer 1 supplied by Kyowa

<sup>2</sup> Alcamizer 5 supplied by Kyowa

<sup>3</sup> supplied by Lagor

shows that the new stabilising system is superior to the compositions containing zinc derivatives (series z, Table 5)

Table 5

	Static thermal stability at 190°C					
	s1	z1	s2	z2	s10	z3
time 0	2	1	2	1	2	1
after 15 min	3	2	3	2	3	2
after 30 min	4	10	3	9	4	9
after 45 min	4		4	10	4	10
after 60 min	5		4		7	
after 75 min	6		5		8	
after 90 min	7		6		8	
after 105 min	7		7		9	
after 120 min	8		7		9	
after 135 min	8		8		9	

The efficiency of the primary stabiliser, object of the present invention, evidently appears from a comparison with formulations in which the main component (zeolite perchlorate or hydrotalcite perchlorate) is replaced by analogous perchlorate-free products (Table 6).

Table 6

	Static thermal stability at 190°C			
	s1	s2	c1	c2
time 0	2	2	4	4
after 15 min	3	3	6	8
after 30 min	4	3	6	9
after 45 min	4	4	7	9
after 60 min	5	4	7	8
after 75 min	6	5	7	8
after 90 min	7	6	8	8
after 105 min	7	7	8	9
after 120 min	8	7	9	9
after 135 min	8	8	10	9

The improvement that each component effects on the stabiliser composition evidently appears from a comparison with formulations not including one of the components being a part of the stabilising system (Table 7).

Table 7  
Static thermal stability at 190°C

	s1	c3	c4	c5	c6
time 0	2	3	2	2	2
after 15 min	3	5	3	3	3
after 30 min	4	7	5	4	6
after 45 min	4	8	6	5	7
after 60 min	5	8	7	7	8
after 75 min	6	8	7	7	8
after 90 min	7	9	8	8	8
after 105 min	7	9	9	9	9
after 120 min	8	9	9	9	9
after 135 min	8	9	10	9	10

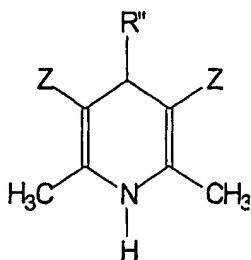
**CLAIMS**

1. A composition capable of conferring high thermal stability upon PVC, comprising essential ingredients:
- A- or X-type zeolite perchlorate or hydrocalcite perchlorate,
- 5 a fatty acid salt of alkaline or alkaline earth metals selected from the group consisting of Li, Na, K, Mg, Ca,
- an organic antioxidant selected out of the classes of alkylidenebisphenols, of esters of 3,5-dicyclohexyl-substituted hydroxyphenyl-propionic acid,
- an organic costabiliser selected from the group consisting of beta-diketonic
- 10 compounds of formula:



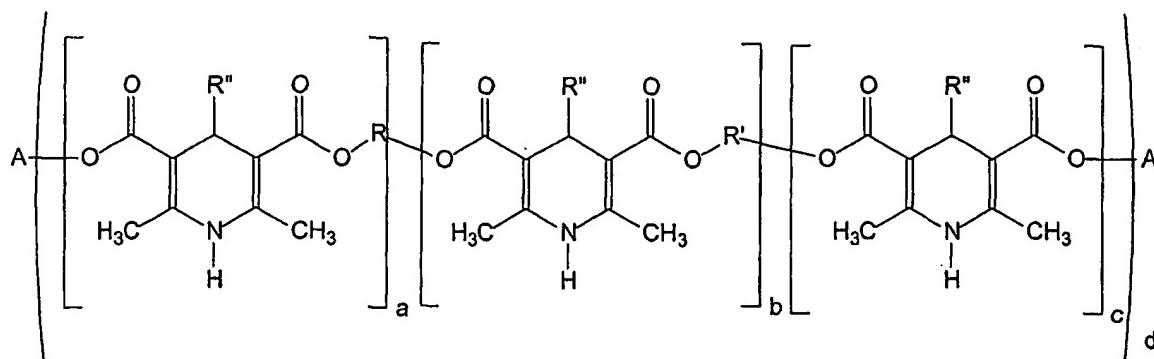
where  $\text{R}_1$  is an alkyl, hydroxyalkyl, alkenyl, phenyl, substituted phenyl, phenylalkyl, cycloalkyl,  $\text{R}_2$  is H, alkyl, alkenyl, phenyl, alkylphenyl,  $\text{R}_3$  has the same meaning as  $\text{R}_1$ ;

- 15 esters of dihydropyridine carboxyl acid of formula:



where Z is  $\text{CO}_2\text{C}_2\text{H}_5$ ,  $\text{CO}_2(\text{n-C}_{12}\text{H}_{25})$ .  $\text{R}''$  is hydrogen, or  $\text{C}_1\text{-C}_{18}$  alkyl or  $\text{C}_2\text{-C}_{18}$  alkoxy carbonyl or  $\text{C}_6\text{-C}_{10}$  aryl;

polydihydropyridine of formula:



where A is non-substituted C<sub>1</sub>-C<sub>22</sub> alkyl or C<sub>1</sub>-C<sub>22</sub> alkyl substituted with C<sub>1</sub>-C<sub>18</sub> alkoxy, C<sub>1</sub>-C<sub>18</sub> alkylthio, hydroxy, acryloyloxy, meta-acryloyloxy, halogen, phenyl, a and b are numbers from 0 to 20,

c is 0 or 1,

5 d is a number from 1 to 6 and conditions d(a+b+c)>1 and a+b>0 are respected,

R and R' are each methylene or phenylene or an alkylene of type

(—C<sub>p</sub>H<sub>2p</sub>—X—)<sub>t</sub>C<sub>p</sub>H<sub>2p</sub>—,

p is a number from 2 to 18,

t is a number from 0 to 10,

10 X is oxygen or sulphur,

R'' is hydrogen or C<sub>1</sub>-C<sub>18</sub> alkyl or C<sub>2</sub>-C<sub>18</sub> alkoxy carbonyl or C<sub>6</sub>-C<sub>10</sub> aryl.

said composition being free from heavy metals compounds and Zn.

2. The composition according to claim 1 wherein the zeolite perchlorate contains Na, K, Mg and Ca as cations and has a cavity of 3 to 5 Å in average diameter ( $\varnothing$ ).

15 3. The stabiliser composition according to claim 1 comprising 0.3 to 2.0 parts by wt. zeolite perchlorate or hydrotalcite perchlorate, 0.1 to 1 parts by wt. metallic soap, 0.03 to 0.3 parts by wt. organic antioxidant, in respect of 100 parts by wt. PVC.

4. The composition according to claim 1 wherein zeolite perchlorate or hydrotalcite perchlorate are obtained by treatment of the starting materials with an aqueous solution of perchloric acid or of alkaline or alkaline earth perchlorate.

5. Highly thermostable rigid or semirigid PVC comprising the stabilising composition according to claim 1.

6. The PVC according to claim 5 obtained by mixing, at 190°C in a calender, the 25 starting polymer with the stabilising composition according to claim 1.

## INTERNATIONAL SEARCH REPORT

International Application No  
PCT/EP 02/05397

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 7 C08K13/02 C08L27/06 // (C08K13/02, 3:16, 5:098, 5:134, 5:07,  
5:3432)

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 7 C08K C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 6 136 900 A (KUHN KARL JOSEF ET AL) 24 October 2000 (2000-10-24) claims 1,11,14	1,3-6
X	EP 0 623 555 A (KAISUI KAGAKU KENKYUJO KK) 9 November 1994 (1994-11-09) claims 3,5,7	1,3-5
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A	US 5 872 166 A (BAE KOOK JIN ET AL) 16 February 1999 (1999-02-16) claims 1-5	1-6

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

## \* Special categories of cited documents :

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- \*O\* document referring to an oral disclosure, use, exhibition or other means
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- \*T\* later document published after the International filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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- \*g\* document member of the same patent family

Date of the actual completion of the international search

4 October 2002

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14/10/2002

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**INTERNATIONAL SEARCH REPORT**

Information on patent family members

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